SOLUBILITIES IN THE SYSTEM

GALLIUM-MERCURY

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INTRODUCTION

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CHAPTER I

INTRODUCTION

The existence of two metallic elements which under ordinary conditions are both liquid presented itself as good grounds for the investigation of mutual solubilities. A search through the literature indicated that little is known concerning solubilities in this system. There have been some data published on the solubility of gallium in mercury but essentially none on the solubility of mercury in gallium.

Ramsay[1], in conjunction with his determinations of the molecular weights of metals, mixed gallium and mercury and stated that the gallium dissolved readily in the mercury. However, Puschin, Stepanovic and Stajic[2], after a more careful investigation found that the mutual solubility of mercury and gallium was only very slight. These authors gave no numerical results. Gilfallan and Bent[3] attempted to determine the solubility of mercury in gallium by means of freezing point lowering. Their results indicated that the solubility was immeasurably small.

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[1] W. Ramsay, J. Chem. Soc., 55, 533 (1889).

[2] N. A. Puschin, S. Stepanovic and V. Stajic, Z. anorg. Chem., 209, 330, (1932).

[3] E. S. Gilfallan Jr. and H. E. Bent, J. Am. Chem. Soc., 56 1663, (1934).

It was the purpose of this investigation to determine quantitatively the extent of the solubility of each metal in the other and the effect of temperature changes on the solubility.

Several modes of investigation were attempted. The first utilized was that of measuring the E.M.F. of a concentration cell in an attempt to determine activities and hence concentrations. Although no positive results were obtained by this method due to inconstancy in the voltage readings, the experimental procedure is described in Appendix I.

It was next attempted to adapt a colorimetric analysis technique to the determination of percentages by weight in the amalgam. An outline and short discussion of the method used are given in Appendix II.

The failure of both of these above methods to give satisfactory results necessitated another means of analysis. This involved the mechanical separation of both layers in the amalgam and their determination by direct chemical means.

CHAPTER II

EXPERIMENTAL

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The melting point of gallium has been determined to be 29.780° C ±0.005[4] and the metal has a great tendency to supercool[5]. In order to minimize any effect this supercooling might have on the solubility of the metals, the initial temperature at which the system was studied was 35° C. This temperature was maintained by means of a constant temperature bath equipped with a Sargent circulating heater, mercurial thermoregulator and relay and capable of maintaining temperatures within 0.01° C. The mixture of the two metals to be studied was introduced into this bath. The gallium used in all determinations was obtained from the Aluminum Company of America and was said by the supplier to be 99.95% pure. Spectrographic analysis indicated traces of iron. The mercury used was purified in the conventional manner by washing with nitric acid and water, drying and distilling.

It is a common property of gallium to wet glass[6]. Since glass utensils were utilized throughout the investigation it became necessary to insure against any loss in weight of gallium by its adherence to the vessel walls. For this purpose a weakly acidic solution of gallium chloride ($GaCl_3$) was used. The gallium chloride solution served three purposes. Primarily, it prevented the metal from wetting the vessel

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[4] W. F. Roeser and J. I. Hoffman, J. Research Nat. Bur. Standards, 13, 673-6 (1934), Research Paper No. 735.

[5] Ibid.

[6] N. A. Puschin, S. Stepanovic and V. Stajic, op. cit.

walls; secondly, it kept the metal surface from contact with air which causes rapid oxidation; and thirdly, the weakly acidic nature of the solution prevented any metal hydrolysis.

Known weights of the two components were brought together and after thorough shaking were introduced into the constant temperature bath. The weights of the metals were taken such that an approximately equivalent volume of each was used.

All gallium to be used in this investigation was first treated with a few drops of concentrated HCl which immediately removed any oxide film. An excess amount of water was then added. This served to dilute the acid and caused the reaction:

$$Ga + 3HCl = GaCl_3 + 3/2H_2$$

to cease, leaving the bright, clean metal. This gallium was then stored under $GaCl_3$.

In the actual weighing of the samples, the gallium was withdrawn from stock by means of a medicine dropper and introduced into the previously weighed weighing bottle by forcing it between sheets of filter paper which served to remove all the $GaCl_3$ solution from the metal. The weighing bottles were immediately capped, weighed and additional $GaCl_3$ introduced to cover the metal surface. In this manner, surface oxidation was kept at a minimum.

The weighed metals were placed together under $GaCl_3$ in a thin-walled test tube and introduced into the 35° C bath. The tube was removed periodically and the contents shaken to insure thorough mixing. As it is impossible to distinguish the metal interface by means of

reflected light, separation of the two layers was made in the following way. The metals after having been allowed to equilibrate in the temperature bath were removed and introduced into a capillary burette. This burette was made of thick-walled Pyrex capillary tubing and fitted at the bottom with a straight, one-way stopcock. The upper end of the capillary was flanged and sealed to a glass tube of larger bore which acted as a reservoir into which the equilibrated metals were placed. The overall length of the burette was about 30 cm. Before the metals were introduced, the burette was partially filled with $GaCl_3$ solution to insure no metal-air contact. After the metals were introduced, they were allowed to stand in the enlarged upper portion of the burette for a few seconds so that none of the less dense upper layer became trapped in the capillary portion. The metals were then very slowly drawn into the capillary portion by partial opening of the stopcock. When the entire volume of the metals was in the lower capillary portion, the stopcock was closed. At this point, a steel shot of slightly smaller diameter than the capillary was introduced onto the upper surface of the metals. The shot was then forced down through the mercury-gallium mixture by means of a long, thin glass rod, until the shot was only slightly above the lower level of the metal. The glass rod was withdrawn and the shot allowed to rise. (The steel shot used was a small ball-bearing and was of such a size that it was possible at all times to view it in the capillary although its upward movement was not restricted.) The difference in density between the steel shot (approximately 7.5) and the mercury (13.6) caused the shot to rise in the lower mercury-rich layer, whereas in the upper gallium-rich layer

(density gallium 6.1) the shot could not rise. Numerous tries were made before each separation and in every instance the shot sought the same level.

Thus, the line of demarkation between the layers had been established. Physical separation of the layers was made as follows: The upper gallium-rich layer was withdrawn down to the level of the steel shot by means of an elongated thin glass pipette. This layer was stored under $GaCl_3$ and labeled. The lower mercury rich layer was withdrawn through the stopcock into another vessel containing $GaCl_3$ and labeled. Each layer was then weighed separately. The same precautions were observed in weighing the separated layers as were described previously in the handling of pure gallium. The actual separation was made in as little time as possible in an effort to minimize any cooling effect on the equilibrium concentration.

Chemical analyses were run on portions of the separated layers after they had been weighed. In order that these samples be uniform in nature, the metals were returned separately to the temperature bath so that equilibrium could again be established.

Samples of each layer were withdrawn by use of the burette, weighed and analyzed according to the following scheme. Concentrated HCl was added to each weighed sample and the reaction allowed to go to completion; i. e., all the gallium converted to the chloride. The residue was thus mercury alone. The reaction of HCl on gallium is relatively slow. In order to speed this reaction small lengths of platinum wire were introduced into the acid solution when dissolving the

gallium from the gallium-rich layer. This procedure hastened the reaction considerably. When the reaction had ceased, the acid solution was decanted and the residual mercury and platinum dried with filter paper and weighed. The mercury was then dissolved by concentrated HNO_3 and the platinum weighed. From the difference in these weights, the weight of mercury was established and consequently the percentage composition determined. The results of these analyses are reported in Table I.

Identical procedures were used in determining the equilibrium concentrations in the two layers at a temperature of 100° C. The results of these determinations are reported in Table II.

The validity of the method of analyzing the various amalgams is illustrated by means of a preliminary experiment. Known weights of the pure metals were mixed and the gallium dissolved by concentrated HCl. From the residual mercury weight, the % error between it and the original weight of mercury was determined by several trials, and this error was found never to exceed 1%.

The results which are given in Table I, Appendix III, indicate that at 35° C the gallium-rich layer contains 7% mercury while the mercury-rich layer contains only 1.5% gallium. At 100° C the solubility of the gallium in mercury was increased to only 98.6% while that of mercury in gallium increased to only 8.5%.

CHAPTER III

THEORETICAL DISCUSSION

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THEORETICAL DISCUSSION

The insolubility of these two metals can probably best be explained by the concept of internal pressures. In the liquid state, the proximity of the molecules of the liquid gives rise to strong cohesive forces which are generally considered as being responsible for the principle properties of this state. However, one may consider separate forces as existing in the interior of the liquid; forces which are due to no permanent dipole moment but to temporary dipoles brought about by changes in the relative position of the charged particles which go to make up the atom (i. e., protons and electrons.) The forces resulting from the interaction of such dipoles are generally referred to as dispersion forces[7]. In liquids, it may be supposed there is a balance between these attractive and repulsive dispersion forces which is responsible for that property known as the internal pressure. A thermodynamic expression for this property can be obtained from the following consideration. The quantity $(\partial E/\partial v)_T dv$ is the change in internal energy brought about by an increase in volume at constant temperature and thus may be regarded as the work done in overcoming the internal pressure during the volume change. Mathematically stated:

$$P_i \, dv = (\partial E/\partial v)_T \, dv$$

where P_i = internal pressure, and thus $P_i = (\partial E/\partial v)_T$.

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[7] S. Glasstone, Textbook of Physical Chemistry, (New York: D. Van Nostrand Company, 1940), p. 291.

It can rigorously be proved from thermodynamic considerations that in order for a solution to be ideal the following must hold[9]:

$$\left(\partial(\partial p/\partial T)_v / \partial \ln N_1\right)_{T,P} = 0$$

Thus it is seen that only those liquids having the same value for $(\partial p/\partial T)_v$ can form ideal solutions. Consequently, the magnitude of the differences between the values for this thermodynamic property of the liquids is a measure of the deviation from ideality to be expected for solutions of these liquids.

A statement of the Second Thermodynamic Equation of State is:

$$(\partial p/\partial T)_v = \frac{1}{T}\left((\partial E/\partial v)_T + P\right)$$

Since the internal pressure is usually very large in comparison with the external pressure, (P), the latter can be neglected; furthermore, at constant temperature,

$$(\partial p/\partial T)_v \propto (\partial E/\partial v)_T$$

Therefore, the quantity $(\partial E/\partial v)_T$ is seen to be a measure of non-ideality.

The most suitable method for approximating the internal pressure of gallium and mercury arises from a consideration of the internal heats of vaporization of the two metals. It can qualitatively be said that the internal heat of vaporization is the work required to overcome

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[9] J. H. Hildebrand, Solubility of Non-Electrolytes, Second Edition, (New York: Reinhold Publishing Corporation, 1936), p. 64.

completely the effect of internal pressure. According to J. H. Hildebrand[10],

$$P_i = (\partial E/\partial v)_T \approx L_i/v$$

and L_i, the internal heat of vaporization, can be approximated by

$$L_i = -1400 + 24.5\,T_b$$

where T_b is the normal boiling point of the liquid. The exact boiling point of gallium has not been determined, but it is known to be greater than 1600° C.[11] On this basis, the internal heat of vaporization for gallium, using 1600° C as its boiling point, is found to be 44,600 cal. and for mercury 14,000 cal. The molar volumes for these two metals are: gallium-11.5 cc/mole; mercury-14.9 cc/mole. The corresponding calculated internal pressures are: gallium-160,000 atm. and mercury-38,800 atm.

One can therefore explain the slight solubility of these two liquids on the basis of the extremely large difference in their internal pressures. It must be remembered that the boiling point of gallium is known to be greater than 1600° C. Therefore, the error involved in the uncertainty of the boiling point of gallium would serve only to magnify the difference in the internal pressures.

Internal pressures can also be estimated from the coefficients of thermal expansion and compressibility by the expression:

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[10] Ibid., p. 102.

[11] P. Harteck, Z. phys. Chem. 134, 9 (1928).

$$P_i = T \alpha/\beta$$

where α = coefficient of thermal expansion and β = coefficient of compressibility. From a calculation of the internal pressure of gallium by the above means, it was stated by Gilfallan and Bent[12] that gallium and mercury would be expected to be mutually soluble. However, as Gilfallan and Bent point out, this method of determining the internal pressure of gallium is to a large extent invalidated by the fact that the constants are open to question.

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[12] E. S. Gilfallan Jr. and H. E. Bent, op. cit.

CHAPTER IV

DISCUSSION OF RESULTS

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As a check on the validity of the data, the ratio of the weights of the two layers as determined experimentally was compared with that ratio taken from the equilibrium diagram (Fig. 1). At 35° C, the ratio of the weights of the two layers was 6.4722/3.0988 = 2.1. From the equilibrium diagram, the ratio of the tie-line lengths was 61.6/30.0 = 2.05. The difference in these two values can be attributed, at least in part, to the mechanical loss in weight in successive weighings of the two layers.

At 100° C, the ratio of the weights of the two layers is 6.4404/3.1040 = 2.07. The ratio of the corresponding tie-line lengths is 60.1/30.0 = 2.00. It is thus seen that the data are in fairly good agreement.

CHAPTER V

SUMMARY

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SUMMARY

As can be seen from the data in Tables I and II, mercury and gallium dissolve each other only very slightly. The two liquid metals form immiscible layers which at 35° C have the composition: gallium-rich layer 93% Ga; mercury-rich layer 98.5% mercury. Temperature appears to have little effect on the solubilities of these metals as the composition of the mercury-rich layer at 100° C remains unchanged while that of the gallium-rich layer increases from 7% to 8.5% mercury.

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APPENDIX I

APPENDIX I

In an effort to determine the composition of the two amalgams, it was deemed plausible to attempt measurements of E.M.F. by means of a concentration cell. For this purpose a small H-shaped cell was made from 6 mm. Pyrex tubing. The lengths of the arms were about 8 cm. and the distance between them about 5 cm. Short lengths of platinum wire (diameter 0.05 cm.) were sealed into the bottom of each arm and allowed to protrude 3 mm. into the cell. Enough pure metallic gallium was introduced into one arm to cover completely the electrode, care being exercised to prevent oxidation of the metal. Into the other arm was placed an equivalent volume of the gallium-rich amalgam and the cell placed in the temperature bath which was regulated for 35° C. A solution of $GaCl_3$ was used as the electrolyte. This solution was prepared by the action of HCl on the metal. After the reaction had ceased, the HCl solution was diluted with water and this acid-water constant boiling mixture evaporated until the solution was only slightly acidic. The cell was connected to a Leeds and Northrup, Type K, Potentiometer with a 6 volt storage battery, in series with a variable resistor, as the power source. A Leeds and Northrup galvanometer, catalog number 2420-A, was connected in the conventional bridge-type circuit.

The E.M.F. values obtained by use of the above cell varied considerably and it was impossible to obtain any constant voltage value. There was no visible evidence of a chemical reaction occurring but agitation of the cell had a marked effect on the galvanometer deflection.

It was thought possible that a reduction of the tri-chloride was taking place so that a solution of the electrolyte was allowed to stand with metallic gallium for a prolonged period. Use of this latter electrolyte had no noticeable effect on the variable E.M.F. readings.

APPENDIX II

APPENDIX II

DITHIZONE METHOD FOR DETERMINATION OF MERCURY[13]

Mercury (II) reacts with excess diphenylthiocarbazone in acid medium, (1N H_2SO_4), to yield a keto complex which is soluble in carbon tetrachloride and gives a colored solution. The mixed-color method was used in attempting to determine the composition of the two immiscible layers. By this scheme, weighed samples of each layer were treated with concentrated nitric acid, converting the Hg to $Hg(NO_3)_2$, and reacting this Hg^{++} with a known volume of standard dithizone which converts the Hg^{++} to the mercuric dithizonate. The Beckmann Model DU Spectrophotometer was used in determining the % transmission of these colored dithizonate solutions. Standard curves were prepared by measuring the transmission of samples containing known weights of mercury in the form of $HgCl_2$, and plotting these readings, as logarithms, against the concentration of mercury. The dithizone used was 0.001% (w/v) in analytical reagent carbon tetrachloride. The sensitivity of this dye is such that accurate determinations can be made colorimetrically only in the range 1-15 micrograms. Many analyses were run but reproducible results were not obtained. It is believed that the necessity of diluting the converted samples to the point where the dye was effective introduced considerable error thus causing the invalid results. These results, however, gave some indication of the relative magnitudes of

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[13] E. B. Sandell, Colorimetric Determinations of Traces of Metals, (New York: Interscience Publishers Incorporated, 1941), p. 180.

the solubilities. The values of several of the analyses are given in Table III. The percentages obtained by this method are obviously too high. From the average of seven random readings on each layer it is seen that the difference between the gallium content of the gallium-rich layer and the mercury content of the mercury-rich layer is 6.3 percentage units. Analysis by direct chemical means gives a difference between these two values at the same temperature of 5.5 percentage units. Thus, the colorimetric method gave values whose differences corresponded to the differences obtained by use of direct chemical analysis. However, on the absolute scale these values were obviously in error.

APPENDIX III

APPENDIX III

TABLE I: Liquid-Liquid Equilibria Data for the System Gallium-Mercury 35° C.

Weight Gallium = 3.0577 gm. Weight Gallium-Rich Layer = 3.0988 gm.

Weight Mercury = 6.6534 gm. Weight Mercury-Rich Layer = 6.4722 gm.

Run	Layer Rich In	Weight Sample (gm.)	Weight Mercury (gm.)	% Hg
1	Hg	0.4083	0.4036	98.8
2	Hg	0.7873	0.7774	98.7
3	Hg	0.5692	0.5558	97.8
4	Hg	0.8126	0.8010	98.5
5	Hg	0.7510	0.7366	98.1
6	Ga	0.3687	0.0241	6.6
7	Ga	0.1007	0.0067	6.7
8	Ga	0.4041	0.0305	7.5

TABLE II: Liquid-Liquid Equilibria Data for the System Gallium-Mercury at 100° C.

Weight Gallium = 3.0577 gm. Weight Gallium-Rich Layer = 3.1040 gm.

Weight Mercury = 6.6534 gm. Weight Mercury-Rich Layer = 6.4404 gm.

Run	Layer Rich In	Weight Sample (gm.)	Weight Mercury (gm.)	% Hg
1	Hg	0.8370	0.8258	98.6
2	Hg	0.8200	0.8090	98.6
3	Hg	0.8518	0.8400	98.6
4	Ga	0.2133	0.0183	8.5
5	Ga	0.2944	0.0250	8.5
6	Ga	0.5042	0.0443	8.8

TABLE III. Results of Spectrophotometric Analyses.

Run	Temp.° C	Layer Rich In		% Mercury
1	35	Mercury		89.5
2	"	"		91.4
3	"	"		97.8
4	"	"		89.6
5	"	"		95.6
6	"	"		91.0
7	"	"		90.5
			Ave.	92.2

Run	Temp.° C	Layer Rich In		% Mercury
8	35	Gallium		15.5
9	"	"		14.2
10	"	"		14.3
11	"	"		14.0
12	"	"		13.5
13	"	"		14.0
14	"	"		13.3
			Ave.	14.1

Author's note: The above tabulated results are not considered reliable. Cf. page 12.

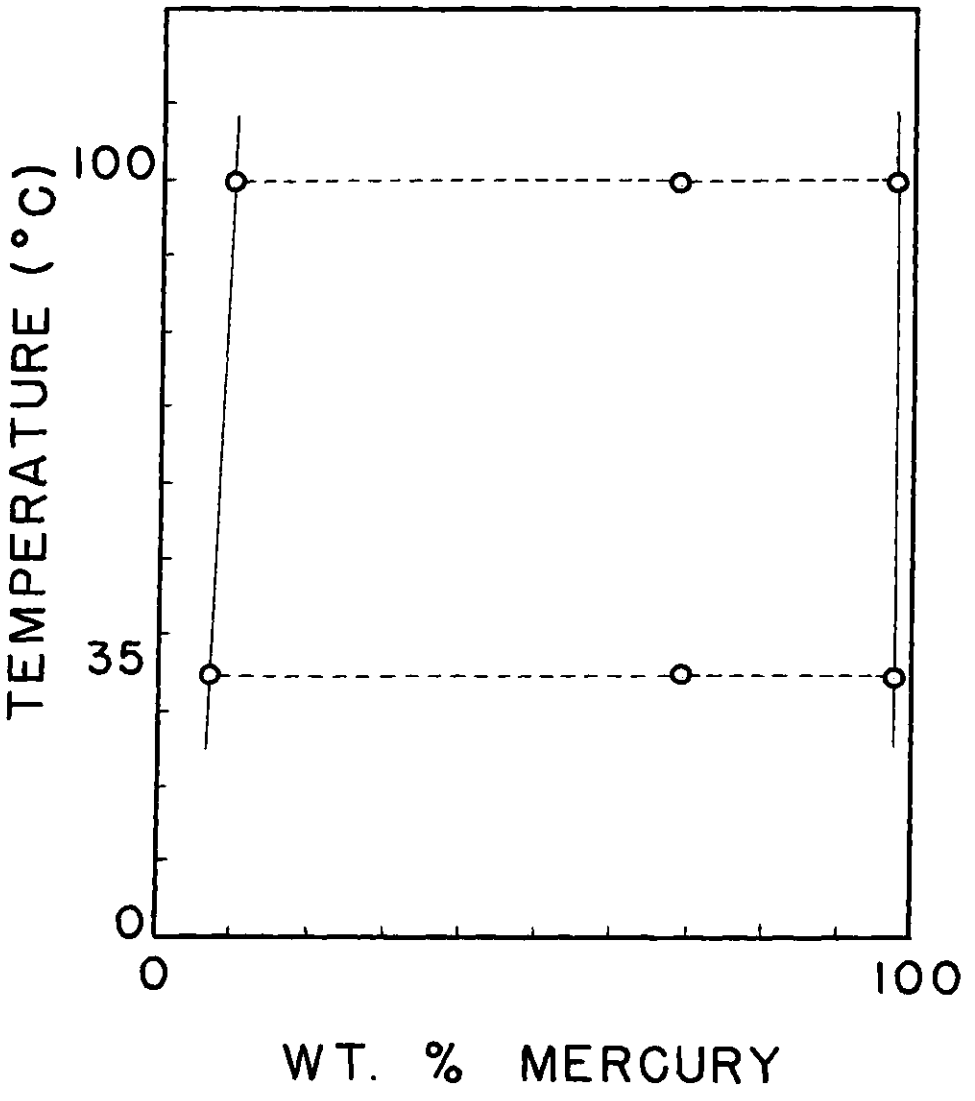

FIG. 1